380 s compared to 3.5 s for water and there was no reduction in the pH and solids content. This thinning out was due to retrogradation of the amylose fraction of the native starch [7]. When the processing temperature was raised to 74°C, a golden yellow adhesive was obtained with no thinning out observed after 4 weeks as earlier observed with adhesive prepared at 60°C. This is probably because the percentage native starch was reduced thereby reducing the 'seeding' tendency [14].
Thick brown pastes of little or no mobility were obtained from the heat degraded starches. The pastes did not draw or thin out even with the addition of 5% (w/v) HCl. The lack of mobility was probably due to the reduction in the length of the starch molecules by heat treatments causing less association.
When the adhesives were applied, very good joints were obtained from paper to paper, to wall, wood, and glasses. No joint was formed between paper and plastic or between smooth surfaces. This is expected because according to *Radley* (1953) mechanical adhesive requires porous surface for keying action. In addition very thin applications were needed to obtain very stable joints.

4 Conclusions

Varing the temperature of steeping, duration of steeping and use of sulphite in steeping cassava pulp affect the physicochemical properties of starch produced. The method of immediate extraction of starch from the grated roots produced starches with high swelling power and peak viscosity, low setback tendency and higher pH which are desirable properties for adhesive formulation with KOH. This method was also most rapid and economical. Adhesives with good stability, colour and applicability was obtained when heated to 74°C. Work is in progress on inprovement of stability, flow properties, and preservation of this adhesive.

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Production and Properties of Starch Phosphates Produced by the Extrusion Process

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Corn starch was phosphated on a Brabender single screw extruder at different extrusion temperatures, sodium tripolyphosphate (STP) concentration and pH of the medium. The highest degree of substitution (DS) was obtained at extrusion temperature of 200°C, STP concentration equal or superior of 1.4g/100mL of water and pH of 8.5. The DS was related to paste clarity while the extrusion process, to the water absorption index and water solubility index, independently of the DS.

Herstellung und Eigenschaften von durch das Extrusionsverfahren gewonnenen Stärkephosphaten. Maisstärke wurde mit einem Brabender-Einschneckenextruder bei verschiedenen Extrusionstemperaturen, Natriumtripolyphosphat-Konzentrationen (STP) und pH-Werten des Mediums phosphatiert. Der höchste Substitutionsgrad (DS) wurde bei der Extrusionstemperatur 200°C, einer STP-Konzentration von 1,4g/100mL Wasser oder höher und bei pH 8.5 erhalten. Der DS stand im Zusammenhang mit der Pastenklarheit, während der Extrusionsprozeß bezüglich Wasserabsorptionsindex und Wasserlöslichkeitsindex unabhängig vom DS blieb.

1 Introduction

Information from the literature suggests that several modifications of starch granules, which increase industrial utilization of starch, are related [1]. Among these modifications esterification of starch with sodium tripolyphosphate (STP) has been employed to obtain pastes, which are clearer, longer, more viscous, cohesive and resistent to retrogradation [2]. Data from the literature show that the properties of such derivatives depend on the type of starch, degree of substitution (DS) and/or the production process [1, 3–7]. According to these authors, in the conventional process, esterification of starch is achieved when a mixture of starch and STP of low moisture content is held for a certain time at high temperatures. The similarities between the temperatures and moisture content employed in the conventional esterification process with those used during the extrusion process [8–12] indicates that the later may be used for starch esterification.
The objective of this work was to investigate the possibility of using the extrusion process to obtain starch phosphate esters. To accomplish this objective the effect of extrusion temperature, STP concentration and pH of the medium on the technological properties: DS, water absorption index (WAI), water solubility index (WSI) and paste clarity of the starch derivative was studied.

2 Materials and Methods

Commercial corn starch from Refinações de Milho Brasil, Ltd. and food grade STP from Monsanto A/S were used throughout the experiments. The method of *Paschall* [1], with some modifications, was used to produce starch phosphate esters by the conventional method of esterification. The method of *Smith* and *Caruso* [13] was used to purify the starch phosphate.

2.1 Extrusion parameters

A Brabender type 20 D-N extruder with vertical feeding was used in the extrusion process. Fixed extrusion parameters were: 3 : 1 compression rate, screw velocity of 130 rpm, a cylindrical matriz with a diameter of 4 mm, first zone temperature of 80°C, feeding rate of 70 g/min and starch moisture content of 16.4%. Variables of the extrusion process were: extrusion temperature, STP concentration and pH of the starch and STP mixture.

2.2 Extrusion temperature

A starch sample of 100,00 g with 12.9% moisture was dispersed in a water solution containing 167 mL of distilled water and 7.60 g of STP. The pH was adjusted to 8.5 and the mixture was recovered by vacuum filtering through a common filter paper and dried to 12.0 to 13.0% moisture content. The dried product was powdered in a mortar, passed through a 35 mesh (0.42 mm) sieve and sprayed with distilled water to increase the moisture content to 16.4%. This mixture of starch and STP, containing 16.4% moisture, was extruded at 130, 145, 160, 175 and 200°C.
The extruded products were dried at 40–45°C for approximately 15 h and powdered to pass through a 1.5 mm diameter sieve. Excess of STP was eliminated with sucessive washings of 65% ethanol water solution and finally with methanol. The purified product was dried at 40–45°C for 2 h.

2.3 Effect of the STP concentration:

Samples of starch (100.00 g) were dispersed in 100 mL of water containing 0,00; 0.20; 0.50; 1.40; 3.00 or 5.00 g of STP. After adjusting the pH to 8.5, these mixtures, were vacuum filtered, dried, powdered and the moisture adjusted to 16.4% as described above. The starch-STP mixtures were extruded at a fixed extrusion temperature of 130°C and the extruded products were dried, powdered and purified as described.

2.4 Effect of pH

The pH of solutions containing 1.40 g of STP in 100 mL of distilled water was adjusted to 5.5; 6.5; 7.5 and 8.5 by the addition of 3.0 N HCl. To these solutions 100.00 g of starch with 12.9% moisture were added and the pH values of the dispersions was confirmed by the method of *Kerr* and *Cleveland* [5]. Vacuum filtering, drying, powdering and moisture adjustement to 16.4% were made as described above. The final mixtures were extruded at a fixed extrusion temperature of 130°C and the extruded products were dried, powdered and purified as described earlier.

2.5 Characterization of the Starch Phosphate:

Purified starch phosphate samples were dialysed against distilled water as described by *Smith* and *Caruso* [13] and used to determine the DS, WAI, WSI and paste clarity. These parameters were determined in purified starch phosphate samples and compared with those of a starch sample without STP extruded with 16.4% moisture, pH of 8.5 and extrusion temperature of 130°C.
DS was calculated by the equation suggested by *Kerr* and *Cleveland* [5].

$$DS = \frac{\%\,Pd - \%\,Pt}{12.8}$$

where: %Pd = Percent of total phosphorous in the derivative on a dry basis,
%Pt = Percent of total phosphorous in the original starch on a dry basis.

Total phosphorous in the samples was determined according to the method of *Smith* and *Caruso* [13]. WAI and WSI were determined by the procedure of *Anderson* et al. [14]. The method of *Kerr* and *Cleveland* [5] was used to determine paste clarity.

3 Results and Discussion

3.1 Technological characteristics:

Table 1 shows the technological characteristics of corn starch, starch phosphate derivative produced by the conventional process and starch extruded at 130°C without STP. Values of WAI, WSI and paste clarity for the corn starch were similar to those found in the Literature [15]. Values for water absorption and water solubility of the corn starch and starch phosphate obtained by the conventional process were lower than those of the extruded starch. These results indicate that during the extrusion process the granules were intensely broken, which increased the amount of soluble compounds and the hydration capacity of the insolubles. On the other hand, the granular structure of the starch was preserved during the conventional phosphating process. Paste clarity of the starch phosphate derivative, as expected, was higher than that shown by the extruded starch.

Table 1.
Characteristics of Corn Starch, Corn Starch Phosphated Conventionally and Extruded Corn Starch at 130°C Without Sodium Tripolyphosphate (STP).

Characteristics	Corn starch	Corn starch phosphated conventionally	Corn starch extrudet without STP
DS	0,0000	0,0030	0,0000
WSI (%)	0,6	0,6	6,3
WAI	2,0	2,1	11,2
Paste Clarity (% transmitance)	28,0	51,0	29,0

DS = Degree of substitution, WSI = Water solubility index, WAI = Water absorption index.

3.2 Extrusion temperature

The effect of the extrusion temperature on DS, WAI, WSI and paste clarity is shown in Table 2. No relationship was observed between extrusion temperature and DS. Maximum DS were observed at 200°C. Increase in the extrusion temperature did not result in significant differences in the WAI. According to *Mercier* et al. [9] and *Mercier* and *Feillet* [10] the WAI reaches a maximum with the increase of extrusion temperature. *Schirmer* [15] observed a parallel increase between WAI and DS for starch phosphates derivatives produced by the conventional process. This was not observed in these experiments with starch phosphates prepared by the extrusion process (Table 2). It is possible that the effect of the extrusion temperature has been counterbalanced by the formation of phosphate-starch esters. The WSI values reached a maximum at 175°C, probably due to the elimination of compounds solubles in 65% alcohol, which were formed at extrusion temperature of 200°C. Formation of oligosaccharides of low molecular weight under these conditions was observed by *Mercier* et al. [9] and *Owusu-Ansah* et al. [11]. Increase in extrusion temperature, up to 175°C, did not cause modifications in the paste clarity. However, the products extruded at 200°C had the highest values for paste clarity.

Table 2.
Effect of the Extrusion Temperature on the Characteristics of Phosphated Starches Produced at Sodium Tripolyphosphate Concentration of 4.5/100 mL of Water and pH 8.5.

Extrusion Temperature	DS	WAI	WSI (%)	Paste clarity (% transmitance)
130	0,0030	11.0	6.3	74.5
145	0,0024	11.9	8.6	74.0
160	0,0027	12.2	10.8	74.5
175	0,0022	11.1	11.8	74.0
200	0,0053	10.8	9.8	83.0

DS = Degree of substitution, WAI = Water absorption index, WSI = Water solubility index.

Table 3.
Effect of Sodium Tripolyphosphate (STP) Concentration on Characteristics of Phosphated Starches Produced at 130°C and pH 8.5.

Concentration of sodium tripolyphosphate (STP) (g/100 mL of water)	DS	WAI	WSI (%)	Paste clarity (% transmitance)
0.2	0.0013	11.9	6.9	45.0
0.8	0.0020	11.1	6.2	63.5
1.4	0.0035	11.9	6.3	74.0
3.0	0.0035	11.2	6.8	74.0
5.0	0.0035	11.5	6.4	74.0

DS = Degree of substitution, WAI = Water absorption index, WSI = Water solubility index.

Table 4.
Effect of pH on the Characteristics of Phosphate Starches Obtained at 130°C and Sodium Tripolyphosphate (STP) Concentration of 1.4 g/100 mL of Water.

pH	DS	WAI	WSI (%)	Paste clarity (% transmitance)
5.5	0.0022	12.0	6.9	45.0
6.5	0.0029	12.0	7.0	60.5
7.5	0.0027	12.2	6.3	66.5
8.5	0.0035	12.3	6.2	73.5

DS = Degree of substitution, WAI = Water absorption index, WSI = Water solubility index.

These results, in conjunction with those of Table 1, show that the extrusion process affected the WSI and WAI while the formation of the phosphate derivative had an influence on paste clarity.

3.3 STP concentration:

Table 3 shows the effect of the STP concentration on the values of DS, WAI, WSI and paste clarity. Increases in the STP concentration, up to 1.4 g/100 mL, were followed by increases in the DS and paste clarity. Thereafter, these values remained constant WAI and WSI remained practically constant with increase of the STP concentration.

3.4 Effect of pH

Effect of pH on DS, WAI, WSI and paste clarity is shown in Table 4. Increase on pH values was followed by increases in the DS and paste clarity. The maximum values of DS and paste clarity were found at pH 8.5 and were similar to those shown in Tables 2 and 3, indicating that these variables are related to each other. Values of WAI and WSI confirmed that these characteristics are related to the extrusion process rather than to the esterification process.

4 Conclusions

The results obtained from this research showed that it is possible to produce starch phosphate with low DS values by the extrusion process. Extrusion temperature of 200°C, STP concentration equal or superior of 1.4 g/100 mL and pH of 8.5 were found as the conditions that resulted in the highest DS. The WAI and WSI were controlled by the extrusion process, independent of the presence of STP. On the other hand, paste clarity was controlled by the DS values.

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